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**A REVIEW OF THE POTENTIAL FOR ACTINIDE
REDISTRIBUTION IN CANDU THORIUM CYCLE FUELS**

by

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Pinawa, Manitoba

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Revue du potentiel pour la redistribution des actinides dans
les combustibles CANDU du cycle de thorium

par

D.J. Cameron

Résumé

La redistribution des actinides résultant de grands gradients de température radiale est une caractéristique reconnue des combustibles $(U,Pu)O_2$ des réacteurs rapides. Un cycle au thorium dans les réacteurs CANDU (Canada Deutérium Uranium) nécessiterait l'emploi de combustibles oxydiques avec deux ou plusieurs composants, ce qui soulève la question de la redistribution des actinides dans ces combustibles. Les mécanismes proposés pour expliquer la redistribution dans les combustibles $(U,Pu)O_2$ sont passés en revue et leur rapport avec les combustibles fondés sur ThO_2 fait l'objet de commentaires. Le combustible considéré en premier lieu est $(Th,U)O_2$ mais il est également question de $(Th,Pu)O_2$.

A ce stade initial de la technologie du cycle de combustible au thorium, il n'est pas possible de considérer quantitativement la question de la redistribution dans des combustibles spécifiques. Cependant, quelques indications peuvent être données aux ingénieurs du combustible, quant aux conditions qui pourraient donner lieu à une importante redistribution.

La conclusion est que la redistribution est probablement peu importante dans le combustible CANDU à haute densité du cycle de thorium dont la température centrale est limitée à 2350 K. Si cette température est dépassée ou si le combustible contient une importante porosité interconnectée, le potentiel pour la redistribution est important et justifie une étude plus approfondie.

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ABSTRACT

Actinide redistribution resulting from large radial temperature gradients is an accepted feature of the technology of fast reactor, (U,Pu)O₂ fuels. A thorium cycle in CANDU (Canada Deuterium Uranium) reactors would require the use of oxide fuels with two or more components, raising the question of actinide redistribution in these fuels. The mechanisms proposed to explain redistribution in (U,Pu)O₂ fuels are reviewed, and their relevance to fuels based on ThO₂ is discussed. The fuel primarily considered is (Th,U)O₂ but some reference is made to (Th,Pu)O₂.

At this early stage of thorium fuel cycle technology, it is not possible to consider quantitatively the question of redistribution in specific fuels. However, some guidelines can be presented to indicate to fuel engineers conditions which might result in significant redistribution.

It is concluded that redistribution is probably of little concern in high density, CANDU, thorium cycle fuel whose centre temperature is limited to 2350 K. If this centre temperature is exceeded, or if the fuel contains substantial inter-connected porosity, the potential for redistribution is significant and warrants more serious study.

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1. INTRODUCTION

To date, CANDU* reactor technology has been concerned almost exclusively with natural uranium, UO_2 fuel. This single component can be treated as an homogeneous entity in many aspects of safety studies, fuel physics calculations, and in mathematical modelling of fuel element behaviour. It seems likely, however, that at some stage in the evolution of CANDU reactor technology a thorium fuel cycle will be introduced⁽¹⁾. This implies a two (or more) component fuel. Currently, it appears that thorium cycle fuels will contain $> 95\%$ ThO_2 , with the fissile component being supplied initially by plutonium (or enriched uranium) and eventually primarily by uranium-233. One exception is the so-called "denatured thorium cycle" where uranium would comprise 10-15% of the heavy elements.

The initial actinide distribution of a multi-component fuel can perhaps be guaranteed, but because of the large temperature gradients present in a fuel, we must know the long-term distribution of the actinide components if we are to be able to predict a number of aspects of thorium fuel performance. This work is an analysis of the possibility of actinide segregation in thorium fuels.

That segregation could occur can be demonstrated by reference to fast reactor technology. Plutonium segregation in fast reactor $(\text{U,Pu})\text{O}_2$ fuels has been well established and extensively studied. O'Boyle et al^(2,3), using electron microprobe techniques, clearly demonstrated the enrichment of plutonium towards the centre of the fuel. The fuel studied had developed a central void due to pore migration, but had not been molten at any stage of irradiation. Lauritzen et al⁽⁴⁾ had previously found plutonium segregation in fuel which had experienced centre melting. Plutonium segregation has subsequently been demonstrated by

* CANada Deuterium Uranium

many investigations and is an accepted feature of fast reactor technology. It has been estimated that plutonium segregation towards the centre of the fuel can impose a penalty of up to 25% on fuel power rating⁽⁵⁾ because of the need to prevent centre melting.

At least two studies^(6,7) have shown that under some conditions redistribution can occur in (Th,U)O₂ fuels. In both studies, the fuel experienced high centre temperatures initially, with columnar grain formation. In one of the studies⁽⁶⁾, apparently reliable quantitative data were obtained on a Th_{0.8}U_{0.2}O₂ fuel which attained an initial centre temperature of approximately 2675 K. A central void was formed by pore migration. The uranium concentration close to the void was approximately 30% of the average concentration, and the uranium concentration peaked at about 180% of the average concentration close to the edge of the region of columnar grain formation. Clearly, a distribution of fissile material such as this will have a significant effect on the physical properties and operating characteristics of the fuel. In the other study⁽⁷⁾, enrichment of uranium close to the central void was observed.

In the case of centre melting, a zone refining type of process on subsequent solidification can account for redistribution. In the absence of melting, two principal mechanisms have been proposed to explain the phenomenon in fast reactor fuels:

1. thermal diffusion resulting from the steep temperature gradients present in the fuel,
2. segregation resulting from evaporation and condensation mechanisms.

The objective of this study is to apply these redistribution models to thorium cycle fuels. To do this some discussion of the models is required. However, their development will not be exhaustively reviewed.

2. REDISTRIBUTION MODELS

2.1 REDISTRIBUTION BY THERMAL DIFFUSION

Thermal diffusion (or the Soret effect) occurs in a multi-component phase exposed to a temperature gradient, resulting in redistribution due to the differences in the lattice energies of the components and their temperature dependencies. When matter flows in the system due to the thermodynamic forces developed by the temperature gradient, there is an accompanying energy flow. This is referred to as the heat of transport. Although the energy transfer is always in the direction of lower temperature, this can be accomplished by flow of matter either up or down the temperature gradient. The heat of transport can therefore be either positive or negative. Equilibrium is achieved when the thermal diffusion is balanced by the normal diffusion resulting from the concentration gradients established.

Bober and Schumacher⁽⁸⁾ present a review of the phenomenon, with emphasis on its relevance to nuclear fuels, based on both irreversible thermodynamics and kinetic theory. It would be superfluous to reproduce this here and we will only present the latter stages of their derivation as it relates to the question of actinide redistribution. The suffixes used by Bober and Schumacher applied to the specific case of a (U,Pu)O₂ fuel; they will be modified here to apply to the general case of an actinide in a thorium fuel. It can be shown that

$$J'_A = -N \left(x_A D_{Th} + x_{Th} D_A \right) \nabla x_A + N x_A x_{Th} \left(\frac{D_A \bar{Q}_A^* - D_{Th} \bar{Q}_{Th}^*}{RT^2} \right) \nabla T \quad (1)$$

where

- J'_A = flux of A in the fixed point reference system,
 N = number of atoms per unit volume of the system,
 x_A, x_{Th} = mole fractions of actinide and thorium respectively,
 D_A, D_{Th} = diffusion coefficient of actinide and thorium respectively,
 $\bar{Q}_A^*, \bar{Q}_{Th}^*$ = effective heat of transport per mole of actinide and thorium respectively,
 R = gas constant,
 T = absolute temperature.

This can be simplified by defining a process heat of transport Q_{ATh}^*

$$Q_{ATh}^* = \left(D_A \bar{Q}_A^* - D_{Th} \bar{Q}_{Th}^* \right) / D_{ATh} \quad (2)$$

where D_{ATh} is the chemical interdiffusion coefficient

$$D_{ATh} = x_A D_{Th} + x_{Th} D_A \quad (3)$$

Q_{ATh}^* can be determined experimentally from measured concentration gradients. The flux equation (1) can then be reduced to:

$$J'_A = -ND_{ATh} \left(\nabla x_A + x_A x_{Th} \frac{Q_{ATh}^*}{RT^2} \nabla T \right) \quad (4)$$

Because of the slow diffusion rate of cations in mixed oxide fuels, equilibrium, with $J'_A = 0$, is probably not achieved in the fuel lifetime and the time-dependent actinide profile is obtained by combining (4) with an equation describing the conservation of the actinide⁽⁹⁾. For a radial geometry, with r being distance in the radial direction

$$\frac{\partial x_A}{\partial t} = -\frac{1}{r} \frac{\partial (rJ'_A)}{\partial r} \quad (5)$$

Combining equations (4) and (5) gives a second-order partial differential equation which can be solved by application of suitable boundary conditions. To complete the solution, the experimentally determined quantities $D_{A_{Th}}$ and $Q_{A_{Th}}^*$ must be obtained.

2.2 REDISTRIBUTION BY VAPOUR TRANSPORT

Rand and Markin⁽¹⁰⁾ were the first to point out that, because of the radial temperature gradient, very large vapour pressure gradients of volatile, metal-bearing species could be produced, leading to segregation in a mixed oxide fuel. They showed qualitatively, by considering the vapour species in equilibrium with a (U,Pu)O₂ fuel as a function of temperature and stoichiometry, that in a hyperstoichiometric fuel there would be a dominant transfer of UO_{3(g)} down the temperature gradient resulting in plutonium enrichment at the centre. However, for markedly hypostoichiometric fuels, the vapour would contain a greater fraction of plutonium than would the solid, so that there would be a depletion of plutonium at the centre of the fuel. As outlined previously, it is well established that central enrichment with plutonium can occur, and, more recently, central depletion has been found in fuels with an initial $O:M \leq 1.95$ ⁽¹¹⁻¹³⁾, in agreement with Rand and Markin's predictions. It should be noted that for thermal diffusion to be the explanation for this behaviour, Q^* would have to change sign at $O:M \sim 1.95$.

Two main mechanisms for vapour transport have been proposed: by vapour diffusion along inter-connected porosity initially present or along cracks which form as a result of power transients; and by sublimation across closed pores in the fuel, resulting in pore migration up the temperature gradient and the formation of a region of columnar grain growth. A number of mathematical models of vapour phase redistribution have been proposed⁽¹⁴⁻¹⁷⁾. The models tend to be complex, commonly incorporating the effect of burn-up on stoichiometry, radial oxygen

redistribution and temperature profiles which vary with time. Computer techniques are usually used to calculate results from the models. Such wide-ranging models are obviously necessary for the complete description of actinide distribution in a fuel element under a range of operating conditions. However, for a study such as this, aimed merely at a preliminary assessment of the potential for actinide redistribution in CANDU thorium cycle fuels, the development of such a model would be premature. What is required is a more idealized treatment of the mechanisms to facilitate the comparison of the magnitude of the relative parameters for thoria fuels with those of (U,Pu)O₂ fast reactor fuels.

Olander has performed such an analysis for the case of migration via cracks⁽¹⁸⁾ (or idealized interconnected porosity) in (U,Pu)O₂ fuel. However, it appears that the model he adopts to describe this process is inapplicable to the case of (Th,U)O₂ fuel because of the different evaporation characteristics of the two fuels. For example, it is assumed that UO₃, a volatile form of the major component of the (U,Pu)O₂ fuel, is the only diffusing species in the crack and that diffusion in the solid is very rapid perpendicular to the crack surface, so that the supply of uranium at the crack surface does not enter into the calculations. In thoria fuels, the major component, ThO₂, is relatively involatile, and, at least for (Th,U)O₂ fuels, UO₃ will be the major vapour phase component. However, the supply of uranium at the high temperature crack surface will almost certainly be the limiting factor in redistribution because the rate of radial vapour phase migration will be much greater than the diffusion rate in the solid perpendicular to the crack surface. No other model specifically directed to transport via cracks has been found, although it appears that the treatment of O'Boyle and Meyer⁽¹⁴⁾ is independent of vapour diffusion route.

Most models of redistribution via the vapour phase are based on the phenomenon of pore migration. Bober and Schumacher⁽⁸⁾, qualitatively, and Olander^(9,19), more analytically, present similar models

based on a quasi-steady-state situation represented by Figure 1. This shows the original location of the pore at (z_o, z_o) which moves to (z_t, z_t) at time t . Initially, because of the high vapour pressure of UO_3 in $(U,Pu)O_2$, it is the dominant subliming species and results in a uranium-rich spike. It is assumed that a steady state is attained whereby the plutonium concentration ahead of the moving pore reaches a concentration such that the ratio of the fluxes of U- and Pu-bearing species across the pore is the same as the ratio of average mole fractions of UO_2 and PuO_2 in the solid solution. Thus, the net effect is the uranium-rich spike at the initial pore location, and excess plutonium at the centre of the fuel when the pore completes its migration. Figure 1 shows the concentration profiles of U and Pu in the fuel during the migration.

Olander⁽¹⁹⁾ shows, and Bober and Schumacher⁽⁸⁾ agree, qualitatively, that the extent of redistribution depends on the ratio of the rate of pore migration and the solid-state interdiffusion coefficient. Olander^(9,19) gives the equation

$$x_{Pu} - x_{Pu}^o = x_{Pu} \exp\left(-\frac{V_p}{D_{Pu}} z\right) \quad (6)$$

to describe the plutonium profile ahead of the advancing pore, where x_{Pu} is the plutonium content of the fuel at a distance z ahead of the pore leading surface, x_{Pu}^o is the nominal plutonium content of the fuel, V_p is the velocity of pore migration and D_{Pu} is the diffusion coefficient of plutonium in the mixed oxide.

While this equation might describe the amount of plutonium transported by void migration, it does not represent the complete problem in applying the knowledge gained from fast reactor technology to CANDU thorium cycle fuel. To assess the problem adequately, the extent of pore migration is required, for it matters little what concentration

profiles are established in the vicinity of the pore, if the pore essentially does not move during the lifetime of the fuel. Therefore, models describing pore migration rates are as equally important as the models describing the amount of excess actinide transported.

Nichols⁽²⁰⁾ has reviewed the phenomenon of pore migration by various mechanisms comprehensively, and derives the following equation for migration by vapour transport,

$$V_p = D_g \Omega \alpha_v p_v \Delta H_v \nabla T / (k^2 T^3) \quad (7)$$

where

- V_p = pore velocity,
- D_g = diffusion rate of the vapour in the gas-filled pore,
- Ω = molar volume of the solid,
- α_v = a factor determining the departure from equilibrium of the vapour pressure,
- p_v = equilibrium vapour pressure of the rate controlling species,
- ΔH_v = heat of vaporization,
- ∇T = the temperature gradient within the pore,
- k = Boltzmann's constant,
- T = absolute temperature.

This equation can be used to compare relative rates of pore migration in thoria and (U,Pu)O₂ fuels.

3. IMPLICATIONS OF THE REDISTRIBUTION MODELS WITH REFERENCE TO THORIA FUELS

3.1 THERMAL DIFFUSION

As outlined in the previous section, Q_{ATh}^* , the heat of transport for thermal diffusion in a thorium/actinide oxide fuel, cannot be estimated theoretically, but must be determined experimentally from thermal gradient experiments. Such data do not currently exist. However, the flux of actinide J'_A is, by equation (4), directly related to the chemical inter-diffusion coefficient. The process of actinide redistribution is relatively slow in the (U,Pu) O_2 system, as shown by the curves of redistribution vs. time presented by Bober and Schumacher⁽⁸⁾ which are reproduced in Figure 2. If the inter-diffusion coefficients in the thorium/actinide oxide systems are much lower than those in the (U,Pu) O_2 system, it can be predicted with reasonable confidence that redistribution by thermal diffusion in the thoria fuels would not be a significant problem, particularly in view of the fact that ∇T in the thoria fuels would be expected to be lower due to a larger fuel diameter and a lower centre temperature.

The value of the chemical inter-diffusion coefficient, D_{Pu} , used by Bober and Schumacher is

$$D_{Pu} = 0.34 \exp(-110000/RT) \text{ cm}^2/\text{s}. \quad (8)$$

The plutonium profiles calculated by Bober and Schumacher using this value for the diffusion coefficient and $Q^* = -147 \text{ kJ/mol}$ show redistribution to occur at temperatures above $\sim 1850 \text{ K}$. Furuya⁽²¹⁾ has measured the tracer diffusion coefficients of U in ThO_2 and $(\text{U}_{0.5}\text{Th}_{0.5})\text{O}_2$. The diffusion coefficients calculated were respectively:

$$D_{Pu} = 1.1 \times 10^{-4} \exp(-76400/RT) \text{ cm}^2/\text{s} \quad (2073 \text{ to } 2273) \quad (9)$$

and

$$D_U = 7.59 \times 10^{-4} \exp(-85900/RT) \text{ cm}^2/\text{s} \quad (2073 \text{ to } 2573) \quad (10)$$

The diffusion coefficients as a function of $1/T$ are plotted in Figure 3. Inspection of these data shows that the possibility of uranium segregation in thorium fuels cannot be dismissed simply on the basis of diffusion coefficients, for, although the diffusion of Pu in $(U,Pu)O_2$ is faster in the higher temperature range, the diffusion of U in ThO_2 is faster at the lower temperatures. In normal thorium recycle fuels, the centre temperature is expected to be limited to ~ 2300 K and only the central 55% of the radius is expected to reach temperatures greater than 1850 K, compared with $\sim 70\%$ of the radius which is subject to redistribution in fast reactor fuels. Also, as mentioned previously, the temperature gradient in thorium recycle fuels is expected to be lower. However, Q^* is unknown for transport of U in ThO_2 and could be numerically much bigger than Q_{UPu}^* . Equations (4) and (5), when combined, give a second-order partial differential equation which is best solved by numerical methods. With Q^* unknown, there seems little point in attempting the solution at this stage, particularly as it can be argued that there are grounds for reservations about the value of D_U which is chosen. This arises from the fact that for dilute solutions of uranium in thorium, small changes in total stoichiometry can give rise to large changes in average uranium valence. It can be shown that fission is likely to change the stoichiometry and average uranium valence in the fuel. The ionic radii of U^{4+} and U^{6+} are 0.097 nm and 0.08 nm respectively, and it might be expected that the diffusion rate of uranium in dilute uranium-thorium solutions would be dependent on ionic size and therefore oxidation state. Indeed, Hawkins and Alcock⁽²³⁾ have shown that the diffusion coefficient of uranium in UO_{2+x} is substantially dependent on the value of x . The situation is further complicated by the potential effect of irradiation on the diffusion coefficients and the contention by Matzke⁽²⁴⁾

that much of the data for diffusion coefficients in actinide oxides are two to four orders of magnitude too high. If this is the case, the whole basis for thermal diffusion in mixed oxide fuel systems as propounded principally by Bober and Schumacher⁽⁸⁾ is thrown into doubt. If the diffusion data they used are this much in error and they still manage to derive distribution profiles which correlate with experiment, the approach may be incorrect, since inspection of equation (4) discloses no other parameter which could have such a large compensating error.

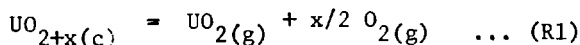
It is expected that the initial fuels used in the establishment of a thorium cycle may be based on thoria containing a small amount of plutonia. The uncertainties outlined above for the analysis of thermal diffusion in (Th,U)O₂ fuels also apply to (Th,Pu)O₂ fuels, with the added complication that to date no data have been found for the diffusion of Pu in ThO₂.

3.2 VAPOUR PHASE TRANSPORT

The tendency for, and rate of, actinide redistribution via the vapour phase depends on the relative and absolute partial pressures of the vapour species above the mixed oxide. Thus, it is necessary to calculate the vapour pressures of the major volatile species in equilibrium with the oxide solid solution of interest. This requires a large amount of thermochemical data. Assessment of the accuracy of thermodynamic data is a major, specialized task beyond the scope of the current investigation. While it is recognized that use of inaccurate data can significantly offset the validity of the calculations, for this preliminary assessment of the magnitude of the problem of segregation, data will be taken uncritically from well-recognized sources in order to calculate the vapour pressures which might be expected in thorium cycle fuels.

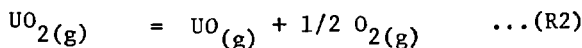
The fuel to be considered has the general formula $\text{Th}_{1-y}\text{U}_y\text{O}_{2+xy}$ and is composed of mole fractions $(1-y)$ of ThO_2 and y of UO_{2+x} . The solid and gaseous species relevant to the calculation of the equilibrium vapour pressures in this system are listed in Table 1 together with their free energies of formation and the sources of the data. The required calculations then follow the lead of Rand and Markin⁽¹⁰⁾ in their work on $(\text{U,Pu})\text{O}_2$ fuels. In that work, it was assumed that the mixed oxides formed an ideal series of solid solutions. This will also be assumed in the present case, although it should be noted that from the work of Aitken et al⁽²⁵⁾, this appears to be less valid for compositions dilute in UO_{2+x} when the oxidation state of the uranium is higher than it is for the same compositions when close to stoichiometry.

The calculations are as follows:



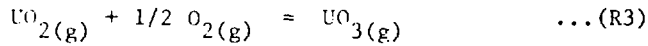
$$\Delta G_{\text{R1}}^{\circ} = -RT \ln \frac{P_{\text{UO}_2} \cdot P_{\text{O}_2}^{x/2}}{y}$$

$$\log P_{\text{UO}_2} = (-\Delta G_{\text{R1}}^{\circ} - x/2 \Delta \bar{G}_{\text{O}_2}^{\circ})/4.575T + \log y \quad (11)$$



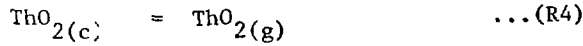
$$\Delta G_{\text{R2}}^{\circ} = -RT \ln \frac{P_{\text{UO}} \cdot P_{\text{O}_2}^{1/2}}{P_{\text{UO}_2}}$$

$$\log P_{\text{UO}} = (-\Delta G_{\text{R2}}^{\circ} - 1/2 \Delta \bar{G}_{\text{O}_2}^{\circ})/4.575T + \log P_{\text{UO}_2} \quad (12)$$



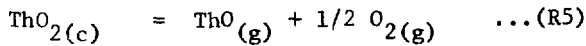
$$\Delta G_{\text{R3}}^{\circ} = -RT \ln \frac{P_{\text{UO}_3}}{P_{\text{UO}_2} \cdot P_{\text{O}_2}^{1/2}}$$

$$\log P_{\text{UO}_3} = (-\Delta G_{\text{R3}}^{\circ} + 1/2 \Delta \bar{G}_{\text{O}_2}) / 4.575T + \log P_{\text{UO}_2} \quad (13)$$



$$\Delta G_{\text{R4}}^{\circ} = -RT \ln \frac{P_{\text{ThO}_2}}{(1-y)}$$

$$\log P_{\text{ThO}_2} = -\Delta G_{\text{R4}}^{\circ} / 4.575T + \log (1-y) \quad (14)$$



$$\Delta G_{\text{R5}}^{\circ} = -RT \ln \frac{P_{\text{ThO}} \cdot P_{\text{O}_2}^{1/2}}{(1-y)}$$

$$\log P_{\text{ThO}} = (-\Delta G_{\text{R5}}^{\circ} - 1/2 \Delta G_{\text{O}_2}) / 4.575T + \log (1-y) \quad (15)$$

It can be seen that except for the equation for the pressure of $\text{ThO}_2(\text{g})$, the oxygen potential of the system $\Delta \bar{G}_{\text{O}_2}$ enters into the calculations, and that this must be specified as a function of x and y.

Here we encounter some conflict. Roberts⁽²⁷⁾, and Roberts and Markin⁽²⁸⁾ contend that as y becomes small, $\Delta\bar{H}_{O_2}$ changes rapidly, whereas for $y > 0.20$, this function is the same as for pure UO_2 . The partial molar entropy \bar{S}_{O_2} varies less significantly at low values of y . Roberts and Markin use arguments based on nearest neighbour interactions, quite convincingly, to explain these results. On the other hand, Tanaka et al⁽²⁹⁾ present results which suggest that $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ can be related to the average uranium valence of the solid solutions for all values of y . This suggests that a minimum value of $\Delta\bar{H}_{O_2}$ is approximately -250 kJ/mol, compared to a value of -42 kJ/mol suggested by Roberts and Markin for very dilute solutions. The choice of oxygen potential values represents a significant source of error in the calculations which can lead to an order of magnitude error in some calculated vapour pressures involving this parameter. It is not possible to resolve this conflict from the published information. In this work, the best fit data published by Tanaka et al have been used, since it is felt that the reasons proposed by Roberts and Markin to explain the rapid changes in $\Delta\bar{H}_{O_2}$ at low values of y are less valid when the departure from stoichiometry is small. Moreover, in the proposed fuel, it is unlikely that high values of \bar{V}_U will be attained. It should also be remembered that the $\Delta\bar{G}_{O_2}$ values calculated in this study are extrapolated far beyond the temperatures at which the data were measured. The values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ read from the curves of Tanaka et al are presented in Table 2.

A computer program was written to calculate the vapour pressures of the major actinide-containing species according to the scheme presented above using the tabulated data. The results calculated for a fuel of composition $Th_{0.97}U_{0.03}O_{2+0.03x}$ are presented in Figures 4 to 6 for temperatures of 2000, 2400 and 2800 K respectively. By far the dominant vapour species at all temperatures is UO_3 , and the vapour pressure of this component is sufficiently high to cause rapid vapour phase migration down the radial temperature gradient in a fuel. Even at this low uranium

loading, the ratio of U:Th in the vapour at a fresh fuel surface is high, leading to preferred uranium transport to colder regions. The ratio does decrease, however, as the temperature increases.

It has been pointed out previously that the more widely accepted mechanism for vapour phase redistribution involves migration of lenticular voids up the fuel temperature gradient. Because the concentration of uranium at the hot side of a void will be rapidly reduced by sublimation of UO_3 across the void, the rate of void migration in this fuel will be controlled essentially by the vapour pressure of ThO_2 at the hot surface, according to equation (7). For an order of magnitude calculation, there is little point in trying to solve equation (7) numerically, since most parameters except p will be similar whatever the fuel. Rather, it is as instructive to compare the vapour pressure of ThO_2 (the species responsible for pore migration in a thorium cycle fuel) with that of the species determining migration rates in some other types of fuel, as is done in Figure 7. It can be seen that for a given vapour pressure in a $U_{0.80}Pu_{0.20}O_{2.00}$ fuel⁽¹⁶⁾, the vapour pressure of ThO_2 reaches the same value at a temperature approximately 400 K higher. A UO_2 fuel will have approximately the same total pressure as the $(U,Pu)O_2$ fuel. Thus, all other things being equal, a temperature differential of ~ 400 K should be applied to the observed fuel restructuring temperatures in UO_2 and $(U,Pu)O_2$ fuels to determine the temperature at which restructuring will become significant in thorium fuels. The work of Christensen⁽³⁰⁾ shows that in UO_2 and $(U,Pu)O_2$ fuels, restructuring occurs in reasonable times at temperatures above ~ 1925 K. Thus, in thorium fuels, restructuring via void migration would not normally be expected below ~ 2300 K. Of course, a rigorous treatment of the problem would be much more complex, involving estimation of fission gas pressures within voids, etc. However, the centre temperature of sintered pellet thorium fuel for CANDU reactors is expected to be less than 2300 K⁽³¹⁾. Accordingly, it is likely that only a small fraction, if any, of the fuel would experience restructuring which would result in uranium segregation. The work of Bain⁽³²⁾, who found only small amounts of columnar grain growth

in a $\text{Th}_{0.98}\text{U}_{0.02}\text{O}_2$ fuel at a temperature of ~ 2570 K, indicates that this estimate is conservative.

Because the pressure of UO_3 generated by the fuel can become significantly large, even at 2000 K, interconnected porosity or cracks could allow sublimation of UO_3 to the outer regions of the fuel. A possible schematic model for this process is shown in Figure 8. In this model, uranium ions diffuse to the crack surface in the hot regions of the fuel, UO_3 migrates down the temperature gradient, condensing on the colder surfaces, and the uranium ions then diffuse into the solid. To complete the circuit, oxygen ("O" in Figure 8) migrates back up the temperature gradient either via solid state diffusion as O^{2-} or via the gas phase in the form of CO_2/CO and/or $\text{H}_2/\text{H}_2\text{O}$ gas mixtures which will exist in the porosity of high temperature fuel⁽¹⁰⁾. In such a system, it is likely that the rate-controlling step will be diffusion of the uranium ions in the solid state.

Computer simulation would be required to analyze this transport process in detail, but it is possible to calculate crudely the rate of uranium loss from the hot regions of the fuel. The problem can be represented as one of diffusion from a semi-infinite medium with an initial uniform concentration. If we assume that gas phase transport is rapid and that the sink to which the UO_3 diffuses is at a low temperature, the UO_3 pressure will be very low, and the concentration of UO_2 at the crack surface essentially zero. Then the amount, M, of UO_2 which has left the solid in time t is given by⁽³³⁾:

$$M = 2 C_o \left(\frac{Dt}{\pi} \right)^{1/2}$$

The fractional loss, f_m , can be derived as a function of the amount of surface per unit volume available, A_c , by eliminating the initial concentration, C_o ,

$$f_m = 2 A_c \left(\frac{Dt}{\pi} \right)^{1/2}$$

At 2300 K, $D \approx 10^{-11} \text{ cm}^2 \cdot \text{s}$, so that

$$f_m = 1.1 \times 10^{-5} t^{1/2} A_c$$

For a cracked fuel, a reasonable assumed value of A_c would be $\sim 10 \text{ cm}^{-1}$. Thus, to evaporate 10% of the UO_2 content would require 8.3×10^5 seconds. For a porous fuel, such as one made by a vibratory compaction process, A_c may be $\sim 500 \text{ cm}^{-1}$. Then the time required to evaporate 10% of the UO_2 would be ~ 330 seconds. The time required for significant redistribution in the cracked fuel is probably large relative to crack healing rates at this temperature, but the time calculated for a porous fuel is sufficiently small to indicate that redistribution may occur in the early life of such a fuel.

4. SUMMARY AND CONCLUSIONS

It is apparent from the foregoing that, with certain provisos, the potential for actinide redistribution is not as great in CANDU thorium cycle fuel as has been found in fast reactor $(\text{U,Pu})\text{O}_2$ fuel. Because of the lower centre temperatures, redistribution by thermal diffusion would affect a smaller fraction of the fuel and, if the latest diffusion data are correct, thermal diffusion is perhaps not viable at all and no redistribution would occur by this mechanism.

Because of the low volatility of the major component of thorium cycle fuels, ThO_2 , redistribution via pore migration, the major mechanism in fast reactor fuels, is rendered much more difficult. A rough comparison on the basis of vapour pressure calculations indicates that temperatures approximately 600 K higher would be required to achieve the same restructuring as is observed in UO_2 or $(\text{U,Pu})\text{O}_2$ fuels. However, the vapour pressure of UO_3 developed in the hot regions of the fuel is sufficient to cause redistribution if transport paths exist in the fuel. If these are present,

the rate of redistribution will probably be controlled by solid-state diffusion and the amount of hot surface available. Vapour phase redistribution in $(\text{Th},\text{Pu})\text{O}_2$ fuels is probably less serious because the vapour pressures of plutonium-bearing species would be much lower than the pressure of UO_3 in a $(\text{Th},\text{U})\text{O}_2$ fuel.

A significant feature of actinide redistribution via the vapour phase in thorium fuels is that the consequences of redistribution are much less severe than for fast reactor fuel and may even be beneficial under some circumstances. The fissile component is displaced away from the centre of the fuel, giving lower centre temperatures than if the reverse were the case. This, combined with the higher melting point of ThO_2 relative to UO_2 and $(\text{U},\text{Pu})\text{O}_2$ reduces concern about centre melting under abnormal operating conditions.

It appears that if high density pellet fuels with a centre temperature limited to ~ 2350 K are used in a CANDU thorium cycle, the question of actinide redistribution is probably of little concern. However, if centre temperatures much above this value are allowed, or if the fuel contains a significant amount of interconnected porosity, even if the temperature is limited to 2350 K, any attempt to model fuel performance must consider radial actinide redistribution in more depth than this study. Also, it is possible that axial vapour phase migration could occur in annular fuels.

This work reveals some gaps in our basic data for fuels based on thorium. For example, the uncertainty in diffusion coefficients in the actinide oxides generally requires resolution, and the conflict evident in the determination of oxygen potential as a function of stoichiometry in thorium-based fuels demonstrates a lack of knowledge fundamental to virtually all aspects of the chemistry of these fuels.

5. ACKNOWLEDGEMENT

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TABLE I

The Thermodynamic Data Used in the Calculation of Equilibrium Vapour Pressures
in $\text{Th}_y\text{U}_{1-y}\text{O}_{2+xy}$

SPECIES	ΔG_f° , J	SOURCE OF DATA
$\text{UO}_{2+x}(\text{c})$	$-(108400 + 136.8 x) + (173.7 + 5.53 x + 151 x^2)T$	Derived from Reference (10) for x from 0 to 0.15
$\text{UO}_2(\text{g})$	$-516700 + 23.87T$	(10)
$\text{UO}(\text{g})$	$-45512 - 46.98T$	(10)
$\text{UO}_3(\text{g})$	$-920600 + 113.68T$	(10)
$\text{ThO}_2(\text{c})$	$1225100 + 183.0T$	(26)
$\text{ThO}_2(\text{g})$	$-553200 + 30.27T$	(26)
$\text{ThO}(\text{g})$	$-64563 - 52.71T$	(26)

TABLE 2

The Values of $\Delta\bar{H}_{O_2}$ and $\Delta\bar{S}_{O_2}$ Selected from the Data of Tanaka et al⁽²⁹⁾ to Calculate the Oxygen Potential as a Function of Stoichiometry

x	$\Delta\bar{H}_{O_2}$, J	$\Delta\bar{S}_{O_2}$, J/mol.K
0.00	-439600	-63
0.01	-238700	8
0.02	-259600	-8
0.03	-263800	-33
0.04	-268000	-50
0.05	-272200	-54
0.075	-280500	-67
0.10	-288900	-80
0.15	-309800	-100

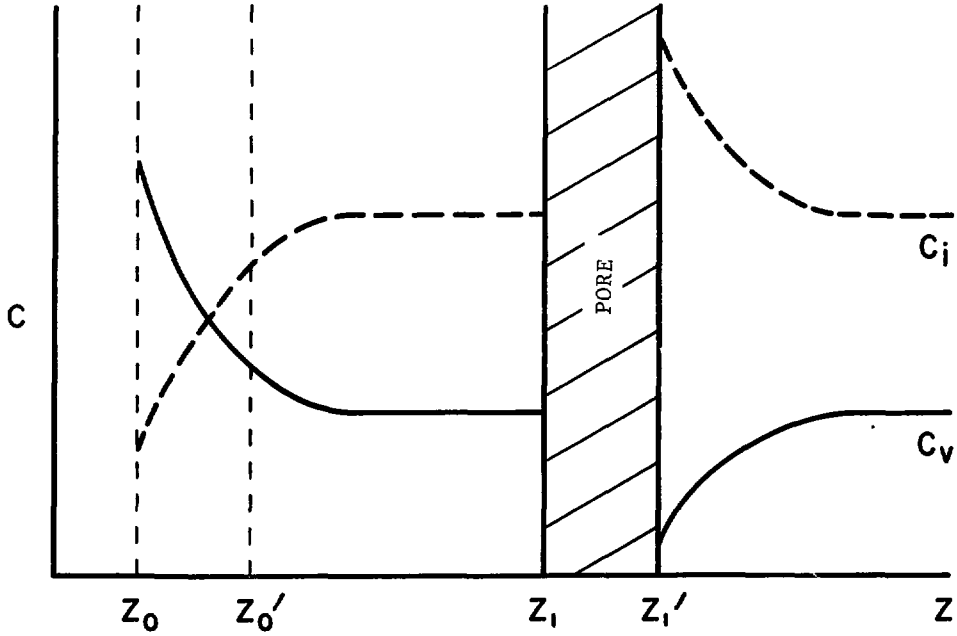


Figure 1: The assumed concentration profiles of the more volatile component, c_v , and the less volatile component, c_i , resulting from a pore moving up a radial temperature gradient from an initial position (z_0, z_0') to a current location (z_1, z_1'). After the example of Bober and Schumacher(8) and Olander(9).

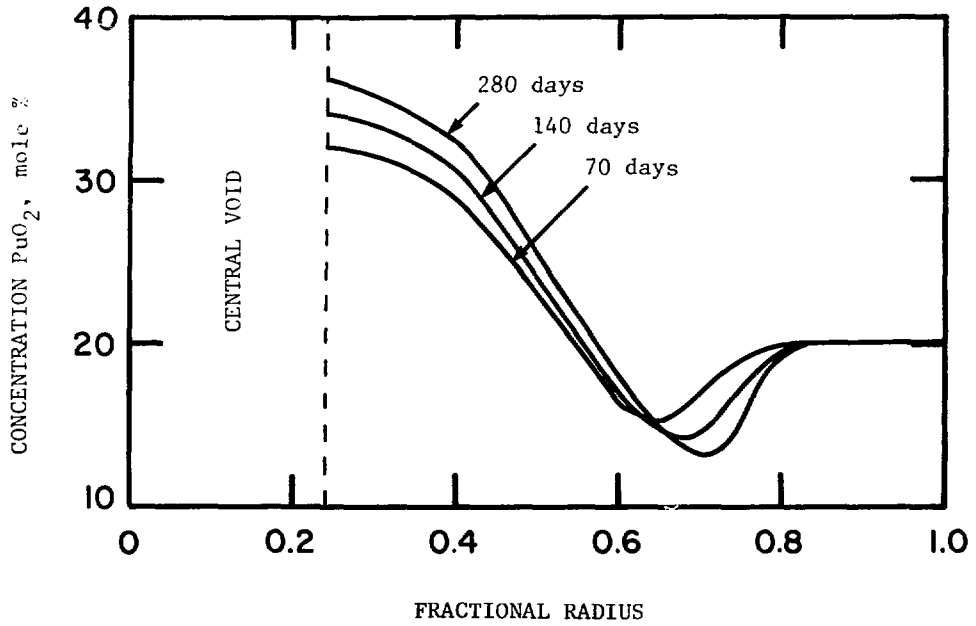


Figure 2: The time dependency of the concentration profile developed in a $\text{U}_{0.8}\text{Pu}_{0.2}\text{O}_2$ fast reactor fuel element with an initial radius of 3 mm at a power rating of 70 kW/m assuming that thermal diffusion is the dominant transport process. After Bober and Schumacher⁽⁸⁾.

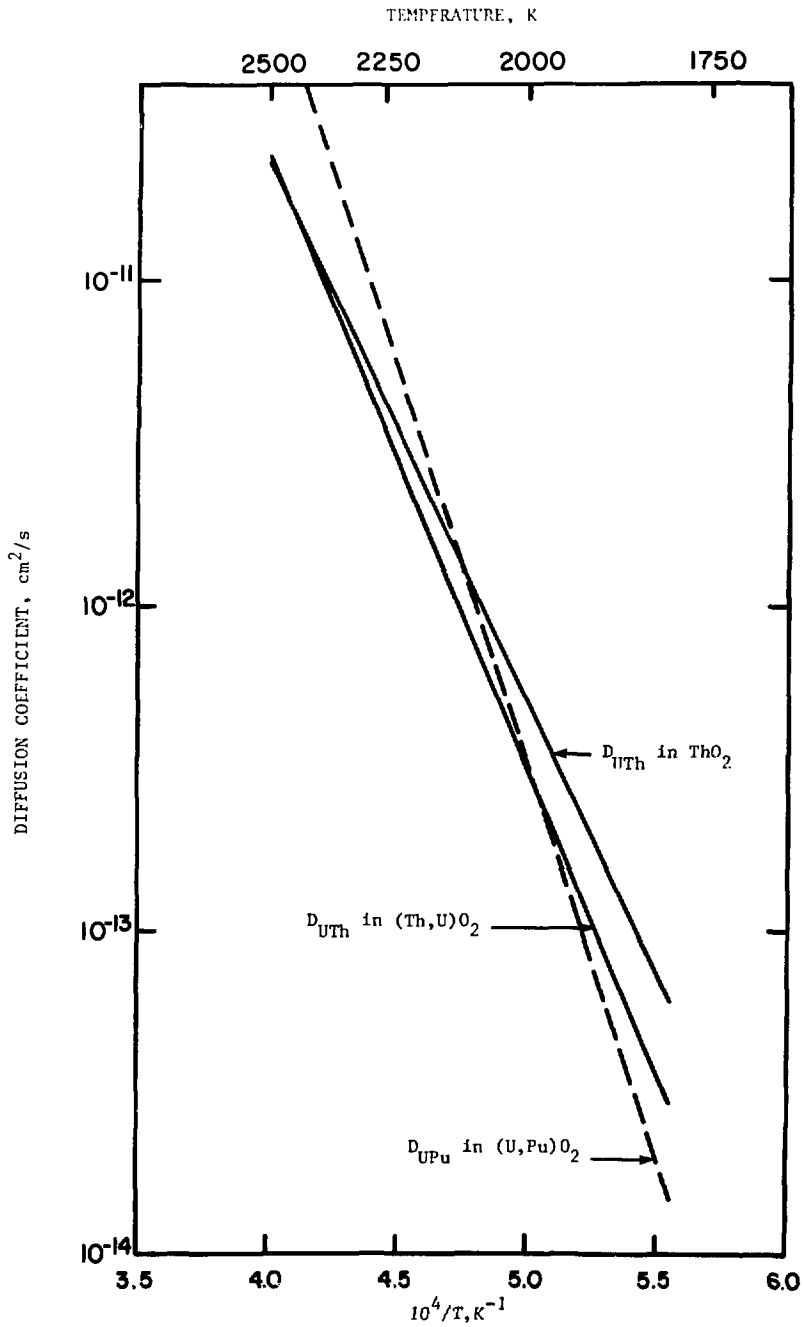


Figure 3: A comparison of the diffusion coefficient of uranium in ThO₂ and Th_{0.5}U_{0.5}O₂ with the diffusion coefficient of plutonium in U_{0.8}Pu_{0.2}O_{2.0}.

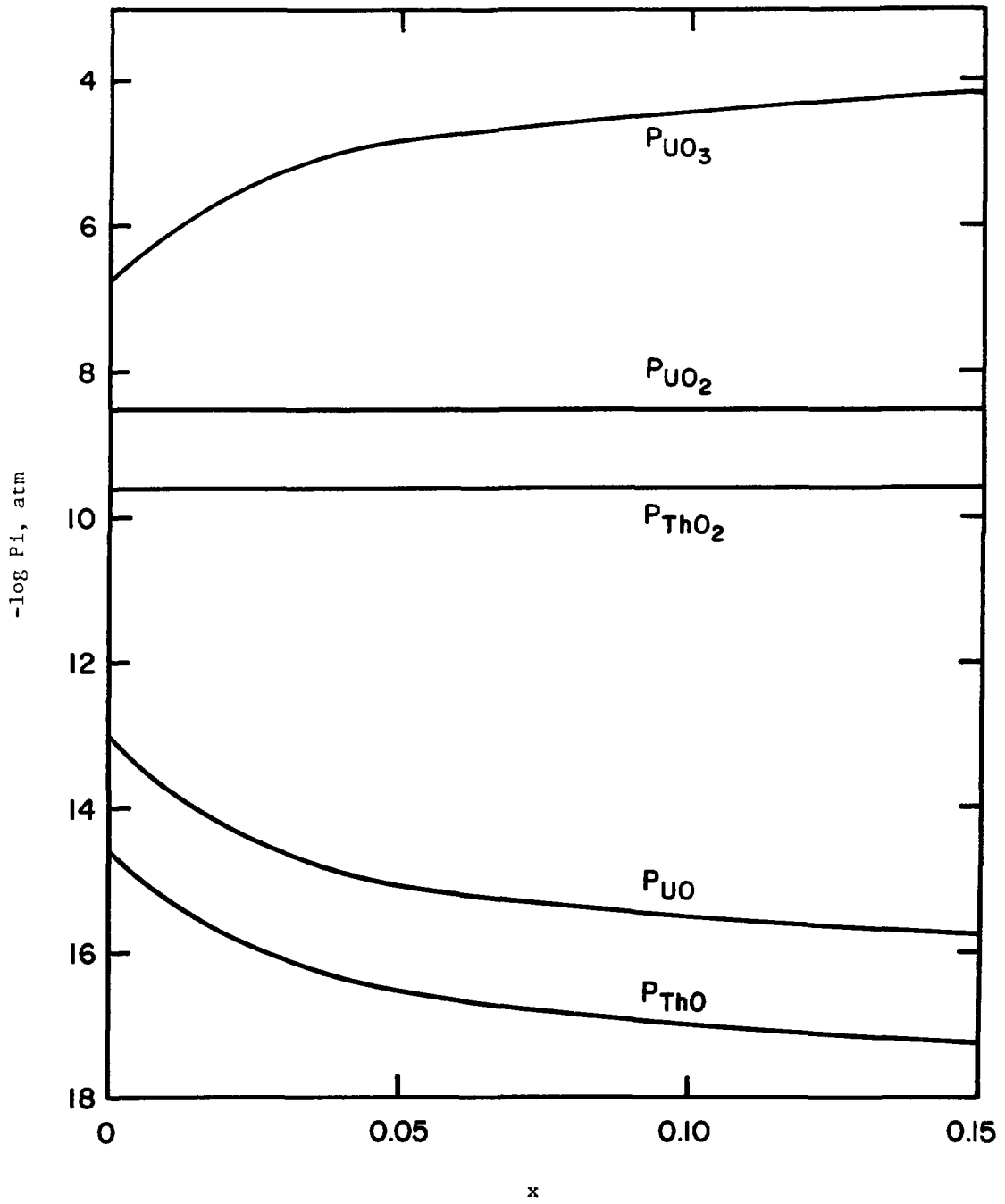


Figure 4: The vapour pressures developed in a $Th_{0.97}U_{0.03}O_2+0.03x$ fuel as a function of stoichiometry at 2000 K.

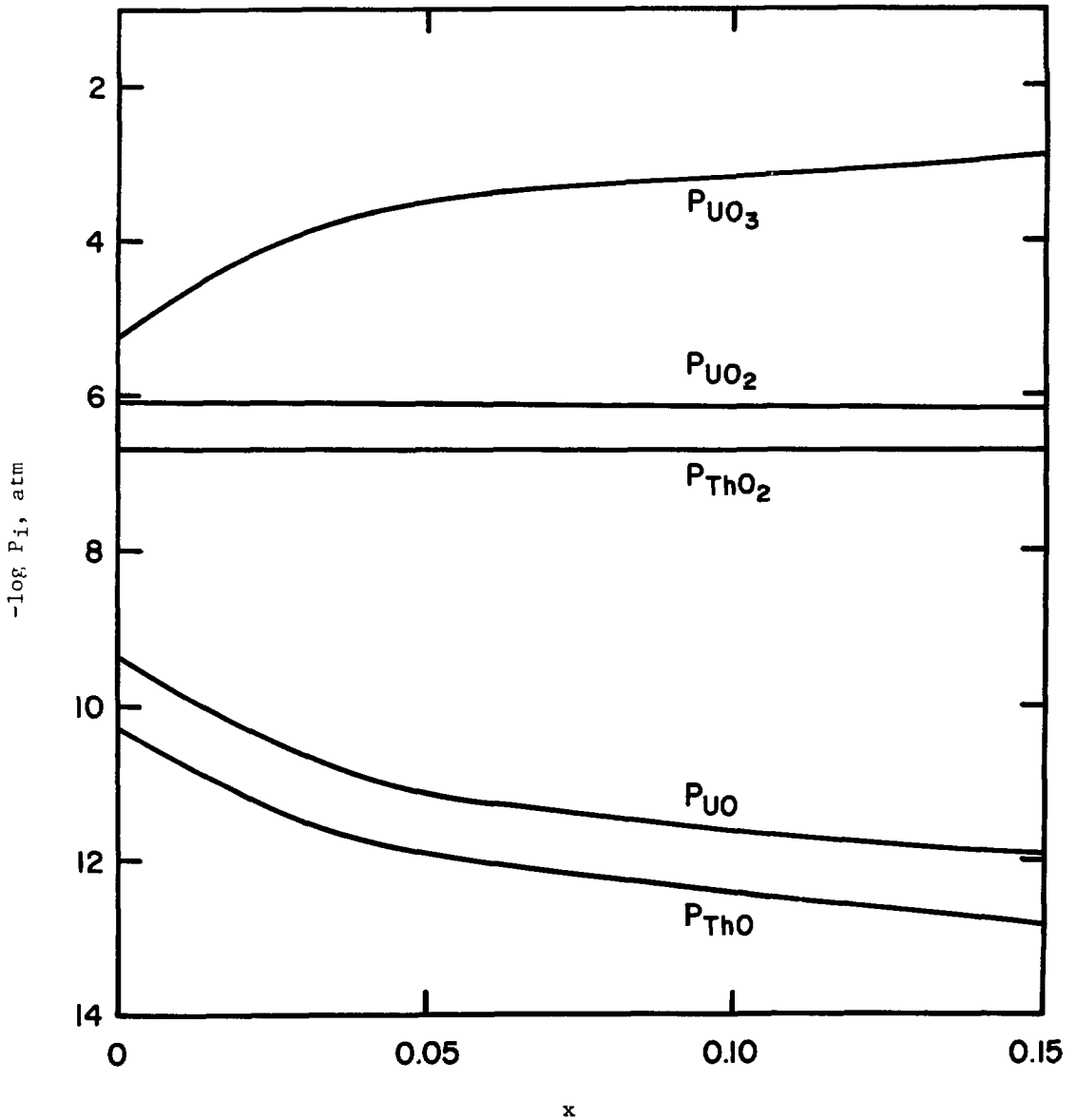


Figure 5: The vapour pressures developed in a $Th_{0.97}U_{0.03}O_{2+0.03x}$ fuel as a function of stoichiometry at 2400 K.

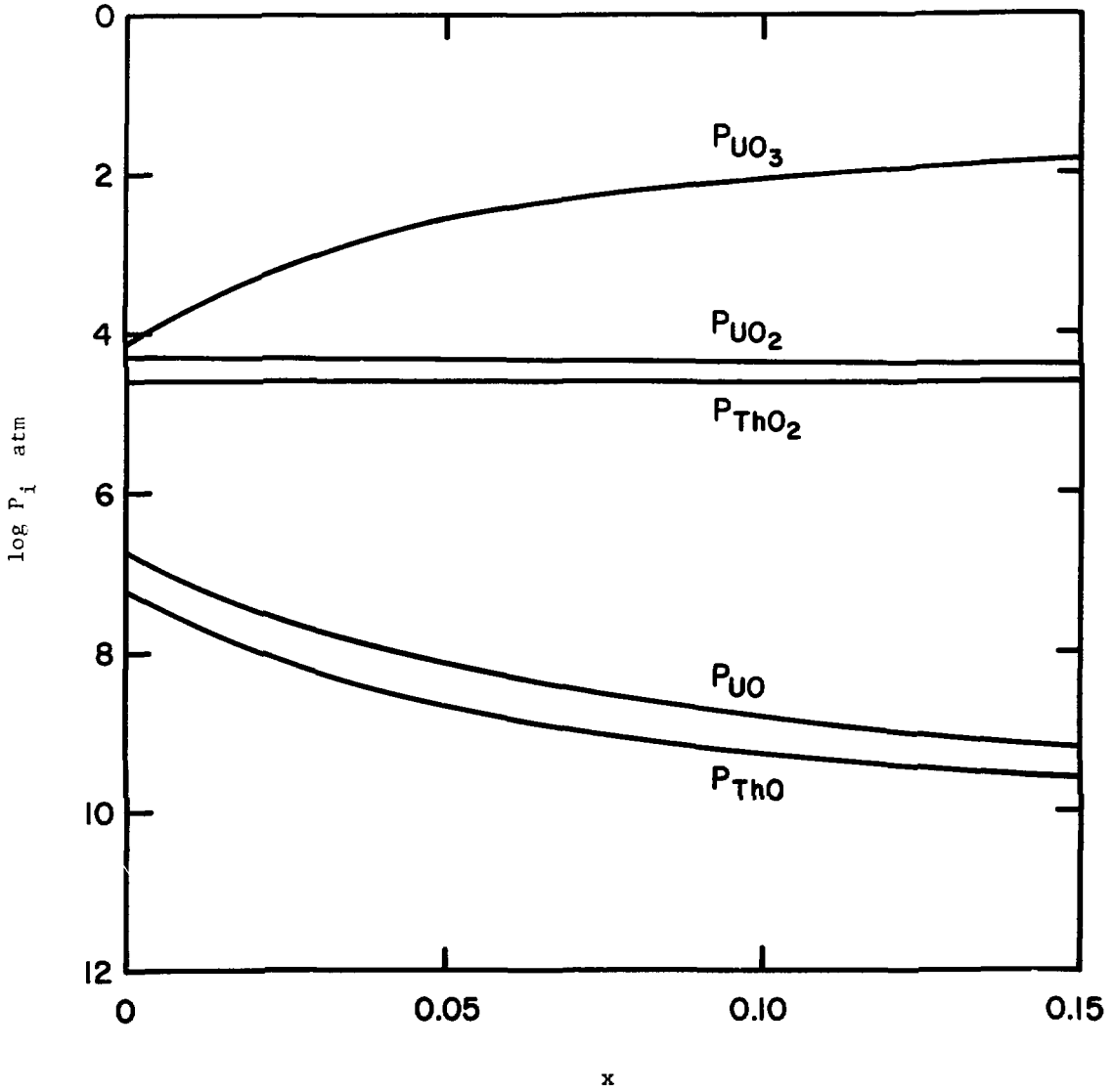


Figure 6: The vapour pressures developed in a $Th_{0.97}U_{0.03}O_{2+0.03x}$ fuel as a function of stoichiometry at 2800 K.

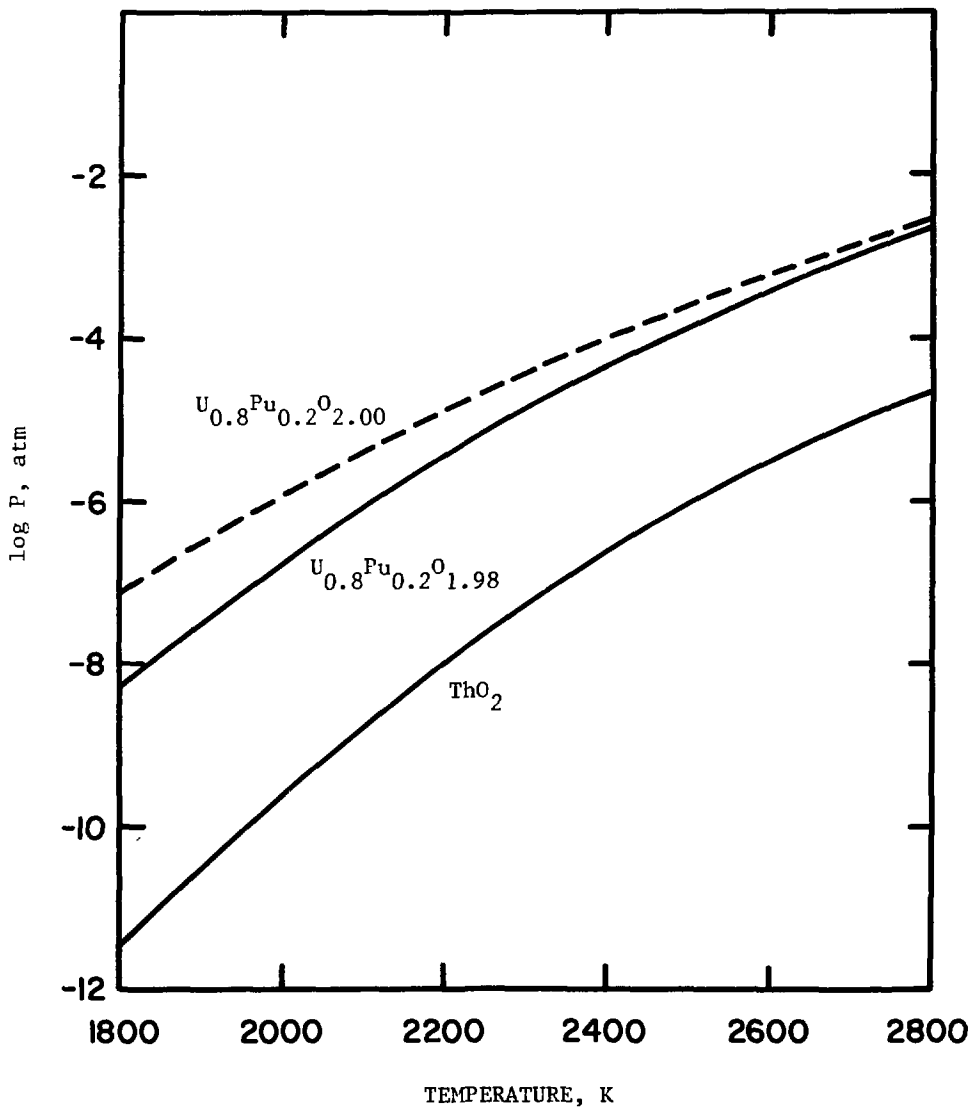


Figure 7: A comparison of the vapour pressure of ThO_2 with the pressure of a fast reactor fuel with two stoichiometries⁽¹⁶⁾.

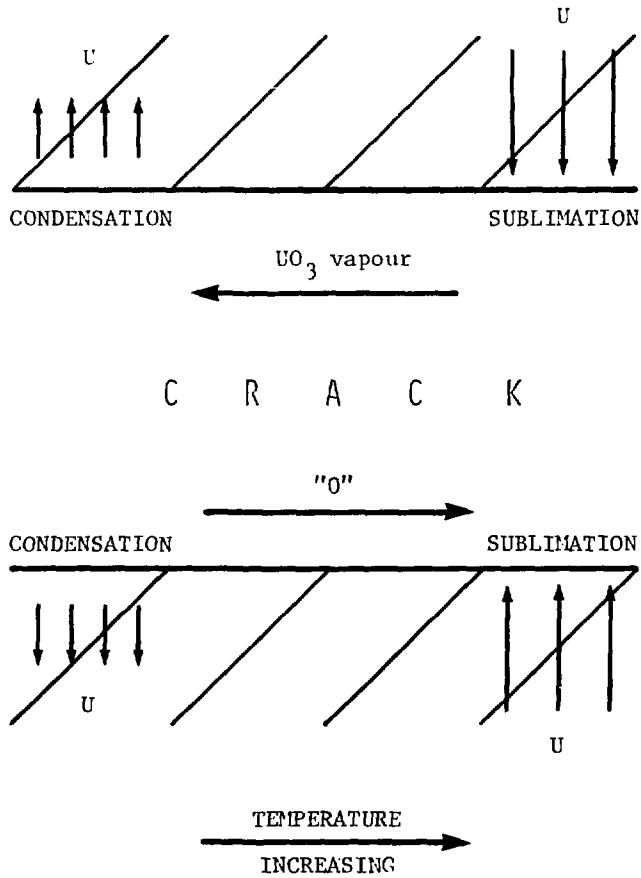


Figure 8: A schematic representation of the transport processes taking place in the transfer of uranium from the hot to cold regions of a (Th,U)O₂ fuel along cracks or interconnected porosity.



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